

CEMENT AND LIME

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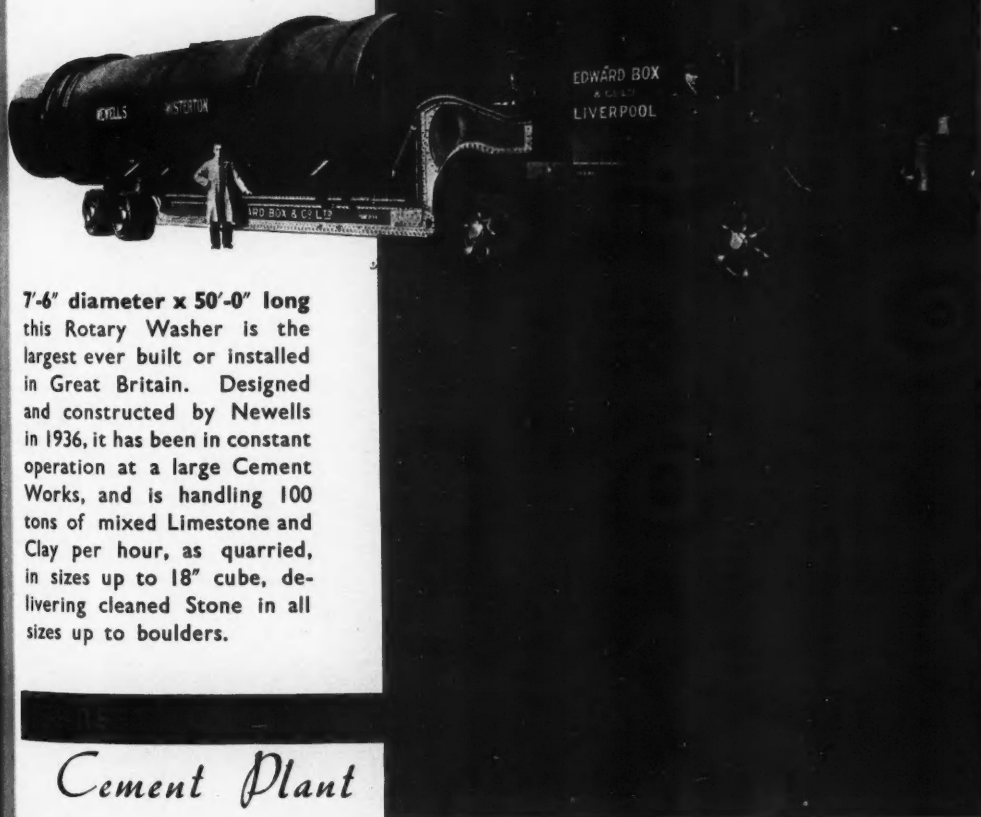
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The Compound Grinding Mill.

As the result of improvements during recent years in burning Portland cement clinker, the procedure of grinding and the machinery used in the grinding process have passed through many stages. The process has become simplified, and a finer product is obtained. Initially the clinker was very rough, and the grinding machinery comprised a crusher and mill stones with either a sieve or a classifier for dealing with the finished product. Later the clinker was smaller, the crushers were cut out, and preliminary and finishing mills were used with or without sieves or classifiers. Sieves and classifiers both proved a nuisance, and this, with the demand for larger grinding units, provided the opportunity for the compound mill. Later experience with this mill led to many improvements and a large increase in the unit size, and to-day mills of the compound type are being adopted as single-process mills in preference to most if not all other types. It may be stated, however, that preliminary mills of possibly several types are being installed as auxiliary units in existing plants in order to obtain better duty and larger output and to avoid scrapping existing machinery.

The compound mill (single-unit mill) is simpler, it can be constructed in larger units, no elevator or conveyor is required for intermediate transfer, and there appears to be no reasonable limit to the size of mill or its output. Mills up to 1,600 h.p. are in service, and there appears to be no reason why they should not reach 2,000 h.p. or even higher; it might be rather more difficult to deal with the increased output, but this problem could no doubt be solved. The range of particle size in the finished product from a compound mill appears to meet the conditions of service better than that obtained from any other mill.

Number of Compartments.

The compound mill as now used is divided into a number of short chambers or compartments with a diaphragm between adjacent chambers forming dividing walls between the chambers and maintaining the segregation of the media. The

number of diaphragms would usually be a matter of convenience or an approximate function of the length of the mill; it would not be practicable to divide a mill 25 ft. long into the same number of compartments as a mill, say, 45 ft. long. The less complete segregation of the media would result in a lower efficiency and an increased h.p. per ton of product of the same or comparable fineness.

Particle Size.

The clinker feed should have a mean dimension of, say, $\frac{1}{4}$ in. A small percentage would be, say, $\frac{1}{2}$ in., and an occasional piece might be as large as $\frac{3}{4}$ in., but the total proportion of these abnormal sizes would be small. No dimension can be assigned to the smallest particles, but a small percentage would probably pass the 170-mesh sieve. The finished product of the mill would have only a small residue on the 170-mesh sieve; the upper limiting dimension would thus be about $1/350$ in., but there would be a small amount of residue above this size.

The size, classification, and distribution of the media should be such as to reduce the varied size of grit from the feed end to the discharge end of the mill, so that a graph of residues would show a reduction over the full length of the mill. Although residue has been referred to, it is possible that the method of classifying cement by its residue will soon become obsolete. Instead, it may become the rule to classify cement by the amount of surface area per pound weight. Possible figures are 650 sq. ft. per pound for ordinary Portland cement and 900 sq. ft. per pound for rapid hardening Portland cement. Comparable figures already in use in the United States are 1,300 sq. cm. per gramme and 1,800 sq. cm. per gramme respectively for comparable cements.

TABLE I.
INCREASING SURFACE OBTAINABLE WITH CUBES OR EQUAL
OF DECREASING DIMENSIONS.

	A	B	C	D	E
Size of cube (in.) ..	1.0	0.1	0.01	0.001	0.0001
Equivalent number per 1 in. cube	1	1,000	1,000,000	1,000,000,000	1,000,000 times
Total surface (sq. in.) ..	6	60	600	6,000	1,000,000
Total surface (sq. ft.) ..	0.0415	0.415	4.15	41.5	60,000
Sq. ft. per lb. (18 1-in. cubes)	0.75	7.50	75.0	750.0	415.0
					7,500.0

The surface of a ball would be rather less than that of a cube of the same dimension, but the number of balls per pound would be greater than that of the cubes and it is not unlikely that the surface of a pound of balls would be very similar to that of one pound of cubes of the same dimension.

The figures in Table I indicate the progressive rate of increase in the amount of surface as the size of particle becomes less; for convenience of calculation and observation the original piece of clinker has been taken at 1 in. cube. This piece of clinker has been followed through in stages, and the final result multiplied by 18 (the number of cubic inches in one pound weight; this figure is in approximate agreement with 96 lb. per cubic foot). It may be assumed that the

possible average particle size of cement having a residue of 5 per cent. on the 170-mesh sieve would be rather greater than 0.001 in., the number of particles per pound weight would be, say, 750 millions, and the surface area would be about 650 sq. ft. per pound. It appears possible that the cementitious value of cement bears some relation to the amount of surface the cement contains. Only a small connection, however, appears possible between a residue-classified cement and its surface, and for this reason some of the figures given in the table are only indicative or approximate and they must be examined in that light; the amount of surface in a cement would be determined by the size of the media used in the later stages of grinding.

Size and Weight of Grinding Media.

The amount of clinker that can be dealt with by a mill is a function of the size and weight of the separate media and also of the total weight of media at the feed end of the mill. The amount of "fines," "flour," or "surface" produced by a mill is a function of the size and classification and also of the total weight of media at the finishing end of the mill. Correctness of size and classification of the media will determine the efficiency of the grinding procedure. Large balls will not produce "fines" or "flour." Small balls will not reduce coarse grit by crushing; they may reduce it by rubbing down or by attrition, but this would involve considerable expenditure of power and result in excessive wear of the media. Effective grinding calls for an appropriate ratio between the size of the grit in process of crushing and the size of media used, and this requirement extends over the full length of the mill.

TABLE II.
ABBREVIATED DATA OF BALLS AND SIMILAR MEDIA.

Diameter or equal (in.).	Weight per ball (lb.).	Balls per lb.	Balls per ton.
$\frac{1}{8}$	0.00230	450	1,000,000
$\frac{5}{16}$	0.00437	230	520,000
$\frac{3}{8}$	0.00750	130	290,000
$\frac{1}{2}$	0.01800	55	125,000
$\frac{5}{8}$	0.06050	16	37,000
1	0.14300	7	16,000
$1\frac{1}{8}$	0.28000	3.5	8,000
$1\frac{1}{4}$	0.48500	2.0	4,500
$1\frac{3}{4}$	0.76000	1.3	3,000
2	1.13000	0.9	2,000
$2\frac{1}{2}$	1.64000		1,350
$2\frac{3}{4}$	2.24000		1,000
3	3.78000		590
4	9.04000		250
5	18.00000		125

NOTE.—An attempt to obtain round figures has lowered the accuracy of the figures, but they should prove sufficiently exact for the purpose in view and for general purposes. The figures may be taken to apply equally well to ball media and to the small-size stubby cylinders now in general use.

The number of impact blows that take place in the grinding process depends largely upon the number of balls or other media that comprise the charge, and for

this reason the size of balls or other media should be kept to the lowest figure practicable; 4-in. balls should not be used if 3-in. or even $3\frac{1}{2}$ -in. are large enough for the duty, and for the same reason 1-in. diameter balls should not be used if $\frac{3}{4}$ -in. are suitable. About two-and-a-half $\frac{3}{4}$ -in. balls have the same weight as one 1-in. ball, and under comparable conditions there would be nearly two-and-a-half times the number of blows from $\frac{3}{4}$ -in. balls as from 1-in. balls. The figures in Table II indicate the advantage of using the smallest size balls or other media in every part of the mill.

When Continental-type ball mills were first introduced into this country a quantity of 5-in. balls was always provided as part of the initial charge, and the same size was invariably used for make-up. At the present time mill operators rarely use balls larger than 4 in. or even $3\frac{1}{2}$ in., but, as the average size of the clinker used for mill feed is probably smaller than it was under the original ball mill conditions, the size of balls used at present is only comparable with that originally used, and even these were large for the duty.

Ball media of 4 in. maximum diameter are now common practice in compound mills when dealing with clinker feed that averages 0.2 in. to 0.25 in. diameter. Media of $\frac{1}{2}$ in. to $\frac{5}{8}$ in. diameter or equal are also used regularly for producing cement grit of the smallest particle size and for finish-grinding the finest cements now being manufactured. A combination of these sizes for mills of the usual diameter, running at 0.75 critical speed and dealing with grit of normal classification, indicates that a media grit ratio of fully 16 to 1 will give good service; this ratio is actually $D = 16d + \frac{1}{2}$ in., where D is the mean diameter of the media and d is the mean diameter of the grit in process of grinding. This rule is more or less arbitrary, but it may be used until something better is evolved. The rule presupposes that the original diameter given for the grit is adhered to, although little difficulty appears likely if occasional pieces of larger clinker pass in with the feed; in any case a few blows with the largest size balls will reduce them to the limiting dimension desired.

The basis and the application of the rule are illustrated diagrammatically in Fig. 1. The upper curve indicates, to scale, the possible reduction in the size of the grit as it passes through a mill of this type, assuming that the operating conditions are good and that the classification of the media is correct, or at least substantially so. The lower curve, to another scale, indicates the size of media, as determined by the rule, suitable for dealing with the particle sizes shown at the various sections. The figures beneath the upper curve show the development of the rule, and there should be no difficulty in following the procedure.

The curve has been extended to cover a very fine product, and it will be necessary to cut off the curve at XX or YY to suit the fineness of the product desired; when this has been done the remaining part of the diagram must be treated as the media-classification diagram for the duty required. The new length of base, to some scale, will represent the total weight of media, and the weight of the assorted sizes will be obtained from the scale of length and the scale of diameters at the left-

hand side. The diaphragms will probably cut through one or more of the quantities, and when that occurs the sub-division must be carried out to discretion. The process is simple, and no difficulty is likely if reasonable care is used.

Reduction in diameter by wear may be rather rapid with the larger sizes, and to provide for this it is suggested that the quantities of the larger sizes be increased by, say, 15 per cent. for the 4-in. to 3-in. sizes, by 10 per cent. for the 3-in. to 2-in. sizes, and by 5 per cent. for the 2-in. to 1-in. sizes; this provision is indicated by the dash line. There is no need for such provision for the smaller sizes.

Types of Diaphragms.

It was stated earlier that the function of the diaphragms was to maintain the segregation of the media. This almost implies that a diaphragm would be required for each size of media, but this would not be practicable and a compromise must

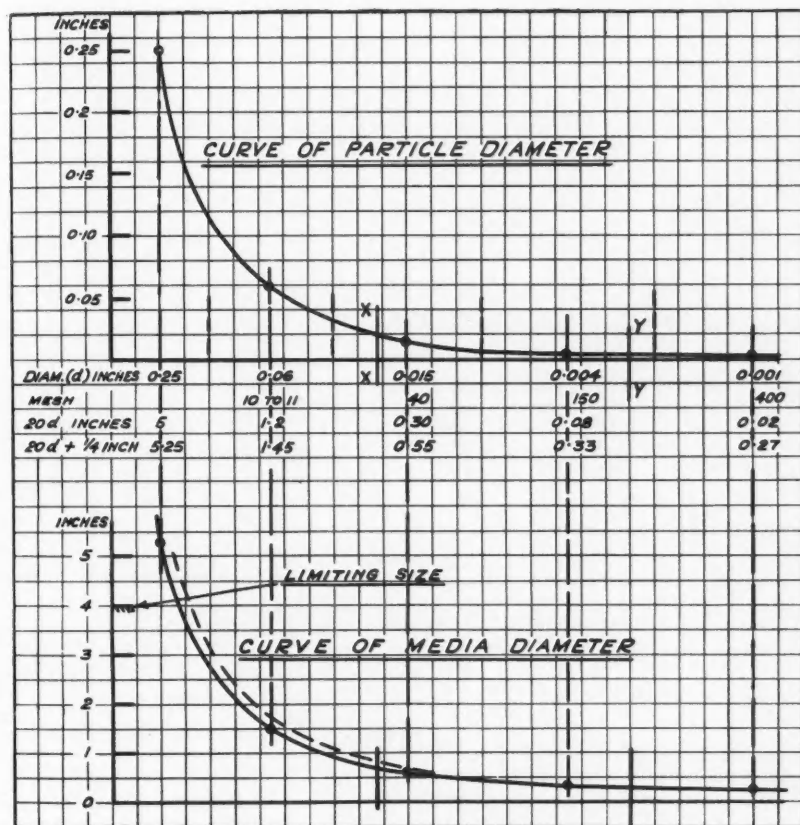


Fig. 1.—Curves of Particle-Media Ratio.

be made. It is convenient to adopt two intermediate diaphragms for mills, say, 25 ft. long, three for mills up to 40 ft. long, and four for mills that exceed that dimension. It will be understood that these numbers are in addition to the diaphragm at the end of the mill which operates as a discharge diaphragm; the number of intermediate diaphragms is thus one less than the number of chambers. The number is arbitrary and can be varied to suit special conditions.

The resistance to the flow of cement through a mill increases with the number of plain diaphragms fitted. Where all the diaphragms are of the plain or non-lifter type, the resistance to flow may easily result in a considerable gradient of the cement in the total length of the mill. This is very objectionable and can only be prevented by fitting diaphragms of the lifter type in some or all positions. The lifter type increases the cost, but it ensures satisfactory performance and keeps the gradient under control and, what is much more important, it definitely prevents the slots on the down-stream face from being blocked up; this blocking-up may prove a very serious difficulty in mill operation and is one result of the use of the small media necessary for the very fine grinding now usual. Lifter diaphragms should be as narrow as practicable consistent with ample lifting capacity. The down-stream face should be generally flat but rugged. The size, number, and location of the slots should ensure a good bed of grit under all reasonable conditions of feed.

Residue-Reduction Graph.

Reference has been made to the residue-reduction graph, which should approximate a hyperbolic curve. The total length of the graph, to some scale, should be in agreement with the length of the mill, and the height, to another scale, should be in agreement with the residue at any point in the length of the mill. The residue that usually matters most is that obtainable on the 170-mesh and the 200-mesh sieves, but the residues on these sieves, when used at the feed end of the mill, would be so high that the figures would be of little value as the media at the feed end of the mill are not suitable for producing "fines." To obtain a complete picture of the performance of the mill it is necessary to use the 8-mesh or the 10-mesh sieve; the 20-mesh or 30-mesh; the 50-mesh or 100-mesh; as well as the 170-mesh and 200-mesh sieves for all samples. The coarser sieves will be most useful at the feed end and the finer sieves at the finishing end.

The indicator diagram obtained from the steam engine, and later from gas and oil engines, showed with exactness what was going on inside the cylinders of these engines; these diagrams could be obtained and examined while the engines were working, and adjustments, based upon or suggested by the diagrams, could often be carried out at the same time. A residue-reduction graph can be constructed from the data obtained from the compound mill, and this graph can give information of considerable value concerning the operating conditions within the mill and so prepare the way for adjustment. It is not possible, however, to do this while the mill is at work. It is necessary to stop the mill and obtain the samples, and the mill can be put into service again while the samples are being classified, the graph drawn, and the adjustments considered. The procedure involves work and

trouble, but it will invariably prove to be well worth while, and moreover it is possibly the only way, or the quickest and best way, of dealing with difficulties or with a mill that is not giving satisfactory service; to say the least, the work involved is much less than that of removing the media, re-classifying, and recharging the mill.

The conditions within a mill are not so stable as those within engine cylinders, owing principally to the varying amount of feed and the variation in hardness or grindability of the clinker. The feeder usually applied to mills of this kind invariably delivers a varying quantity of feed, amounting to, or even exceeding, 5 per cent. above or below the mean quantity. This variation may be caused by a difference in the "flow" characteristic of the clinker and also in the varying height of the clinker in the feed hopper. There appears to be no complete cure for these conditions, but an improvement would probably be effected if a volume feeder or a weighted feeder were used. Some objections would probably be found to both

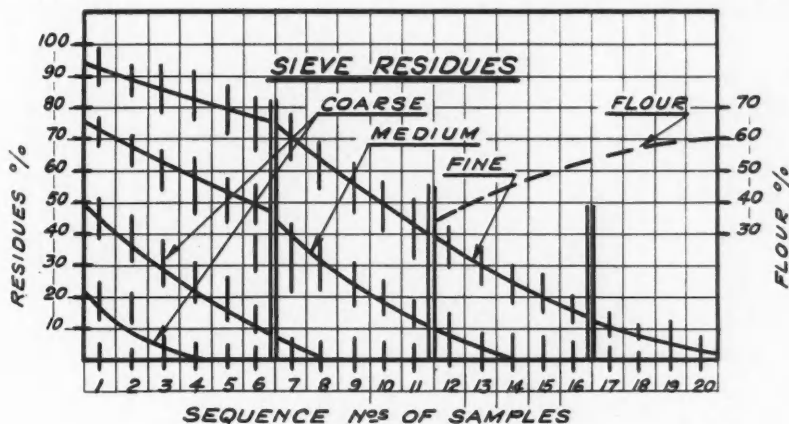


Fig. 2.—Residue-Reduction Graph.

these types, but one or the other would most likely work with a smaller variation than that of the original type. Variation in the hardness of the clinker may be caused by differences in the calcining temperature. It does not appear possible at the moment to burn all the clinker 100 per cent. consistently all the time, but improvements in the burning process are continually being made and no one can say what the early future will bring.

Fig. 2 indicates a typical residue-reduction graph such as would be obtained from a mill working under good and normal conditions. To obtain the data for a graph of this type, carefully-obtained samples would be required and the work of sieving and classification correctly carried out. The samples would be obtained from the mill running under normal feed conditions—the mill having been stopped with the feed on, the covers removed, and the samples obtained from equally divided positions about 18 in. apart; the covers can then be put on and the mill

put into service while the samples are dealt with. If the classification of the media is correct, and the internal condition of the mill is in order, grit reduction, as stated, will be consistent all through the length of the mill. The reduction will be most pronounced at the feed end where the grit was originally of considerable size; the reduction at the finishing end will be apparently at a lower rate, but the number of particles at this point will be much greater and flour will be in process of formation. If the media are of incorrect classification in any chamber, the graph will show at once which chamber it is, and the cause can be deduced. There will probably be a break in the continuity of the curve at the diaphragms—the residue is usually found to be rather lower on the down-stream side.

Generally speaking, the information given by the graph can only be relative or indicative. It will not show whether the mill as a whole is doing good work or not, but it will show which chamber is doing better or poorer work than the others, and by so doing it will suggest or indicate the line of improvement. The usefulness or the efficiency of the mill as a whole can only be determined by a consideration of the weight, fineness and general characteristics of the product and the amount of power (B.H.P.) that has been absorbed in the grinding process. If the media in any chamber are too small for the duty, the residue on the sieves for that chamber will show little if any reduction. If the media in any chamber are consistently large, the residue at the up-stream end will be quickly reduced, but the curve will flatten towards the down-stream end. The former condition may apply especially to the feed end and the latter to the finishing end. A normal residue-reduction curve will always be flatter at the down-stream end owing to the reduced size of the grit and owing also to the fact that most of the work for that size of media has been completed. If the original mean size of the clinker was 0.25 in., and the mean size of the product was 0.0025 in., the mean ratio of reduction would be, say, 100:1; this figure ignores the small amount of over-size clinker in the feed (this ratio of reduction is very large).

The compound grinding mill as described is a very useful machine and can be used commercially for all, or nearly all, grinding duties. It will give a good account of itself if it is correctly treated, and if the range of particle size (residue) in the separate parcels of finished product is not too large. The mill will do its best work if the media are exactly suited for the finished products as illustrated in Fig. 2. General experience with the compound mill indicates that two-stage grinding can only be justified under very special conditions.

The sieves referred to are in accordance with B.S.S. No. 410. Flour is defined, and the elutriator for estimating the amount of flour in a sample is illustrated and its use described in *Portland Cement*, by A. C. Davis (Concrete Publications, Ltd.). With regard to surface, although many experimenters appear to be working on the subject, there does not appear to be a machine or apparatus that is universally acceptable for measuring or estimating the amount of surface in a sample. A good description of the principles involved and the procedure necessary is given in the description of the Wagner "turbidimeter" given in tentative specification C.115-38T of the American Society for Testing Materials, 1938.

Determination of Ferric Oxide in Cement.

A USEFUL paper on titrating mixtures, by Messrs. A. J. Johnson and J. T. Lynn (of the Lehigh Portland Cement Co.), has been published in *Rock Products*.

The authors state that since Knop¹ recommended the use of diphenylamine as an indicator in the dichromate titration of ferrous oxide, and more particularly since King² described the details of a method for the determination of ferric oxide in Portland cement, methods which are essentially due to King have been in use.^{3 4} Gibson⁵ has criticised King's method and suggested its improvement by the use of a different "titrating mixture." Kolthoff⁶ in 1929 called attention to the fact that diphenylamine was not an ideal indicator for this titration. Since then other investigators have discovered that the colour change of diphenylamine is affected by temperature, acidity, and time. Kolthoff and Sarver have made a systematic study of the properties of diphenylamine and diphenyl benzidine,⁷ developed diphenylamine sulphonic acid as an oxidation reduction indicator,⁸ determined the indicator corrections for the three indicators, and described the conditions of acidity, concentration, etc., for their use.⁹ The purpose of the present authors is to call attention to the errors that are apt to arise from the use of diphenylamine in the laboratory and to point out the advantages of diphenylamine sulphonic acid as an indicator.

Diphenylamine Indicator.

Solutions were prepared as described by King except that the dichromate was prepared by dissolving 1.5375 gr. of potassium dichromate per litre of water. The titrating mixture thus prepared is referred to as "King's titrating mixture." A titrating solution was also prepared according to Gibson's directions. This is referred to as "Gibson's titrating mixture."

The dichromate solution was standardised against the National Bureau of Standards standard sample No. 27-B as follows: Three 0.2507-gr. samples of the dried (105 deg. C.) ore were treated with 20 ml. concentrated hydrochloric acid and digested at 80 deg. C. to 90 deg. C. until solution was complete. Solution was hastened by the addition of stannous chloride solution in sufficient quantity so that when the sample was completely dissolved (except for a little silica) the colour was a pale yellow. This solution was diluted to 100 ml., and 10-ml. portions were taken for titration. Three portions were taken from each of the three samples. Each 10-ml. portion was transferred to a 250-ml. beaker, 8 ml. of concentrated hydrochloric acid added and the solution was heated to boiling. The yellow colour of ferric chloride was dissipated by the addition of stannous chloride solution by drops, using one drop in excess. The reduced solution was at once cooled by immersing the beaker in a pan of cold water. As soon as it was cool, 20 ml. of saturated mercuric chloride solution were added and the solution stirred for a minute. Twenty ml. of Gibson's titrating mixture were added, the volume diluted to 100 ml., 5 drops of diphenylamine solution added, and titrated with dichromate.

The average of the nine titrations was taken as the ferric oxide equivalent of the dichromate solution. The results obtained in the standardisation of the dichromate are listed in *Table I*.

TABLE I
STANDARDISATION OF POTASSIUM DICHROMATE SOLUTION

	Ml. $K_2Cr_2O_7$ for Titration		
	Sample No. 1	Sample No. 2	Sample No. 3
Portion No. 1	10.27	10.32	10.40
Portion No. 2	10.27	10.28	10.40
Portion No. 3	10.35	10.30	10.28
Average	10.30	10.30	10.36

Average = 10.32 ml. potassium dichromate solution.

Fe_2O_3 in sample $\frac{(0.2507)(0.9756)}{10} = 0.02446$ gr.

1 ml. $K_2Cr_2O_7$ solution = $\frac{0.02446}{10.32} = 0.00237$ gr. Fe_2O_3 .

Effect of Dilution and Titrating Mixtures.

To determine the relative merits of King's and Gibson's titrating mixtures a stock solution of ferric chloride was prepared. Twenty-five ml. portions of this were treated with 10 ml. of concentrated hydrochloric acid, boiled, reduced with stannous chloride, cooled, treated with 20 ml. of mercuric chloride and 20 ml. of titrating mixture, and then diluted to various volumes with distilled water before titration. The results of these tests are listed in *Table II*. Five

TABLE II
EFFECT OF VOLUME AND TITRATING SOLUTION ON END POINT

Test No.	Ml. $FeCl_3$ solution used	Total volume at start of titration	Kind of titrating mixture used	Ml. dichromate solution required	Distinctness of end point
1 ..	25	90	King	5.30	Fair
2 ..	25	90	King	5.61	Fair
3 ..	25	140	King	7.00	Poor
4 ..	25	140	King	7.00	Poor
5 ..	25	240	King	13.00	Very poor
6 ..	25	240	King	12.20	Very poor
7 ..	25	90	Gibson	5.30	Good
8 ..	25	90	Gibson	5.27	Good
9 ..	25	240	Gibson	5.21	Good
10 ..	25	240	Gibson	5.40	Good

drops of indicator were used for each titration. From the results of these tests it was decided to use Gibson's titrating mixture for the remainder of the tests on diphenylamine.

Effect of Iron Concentration.

A solution of ferric chloride in 3 per cent. hydrochloric acid was prepared of such strength that 10 ml. of solution required 10 ml. of dichromate for titration.

Since the dichromate solution was standardised against an amount of Sibley iron ore which required 10.32 ml. of potassium dichromate for titration, the ferric oxide content of the ferric chloride solution was calculated from the results of titrating 10-ml. portions. Using the ferric chloride solution as a standard, several samples of varying ferric oxide content were tested. The final volume, before titration, was brought to 100 ml. for each test (Test No. 18 required concentration of the 73 ml. sample before reduction). The results are listed in *Table III*. To each sample was added 10 ml. of hydrochloric acid; the solution was boiled; reduced with stannous chloride; cooled; 20 ml. of mercuric chloride, 20 ml. of Gibson's titrating mixture, and 5 drops of indicator were added, and the volume diluted to 100 ml. before titration.

Discussion of Results with Diphenylamine.

Each of the tests mentioned in *Table III* was made by an experienced analyst. Where duplicate tests were made the check results were obtained by a different analyst using the same burette and solutions.

TABLE III
EFFECT OF IRON CONCENTRATION ON END POINT USING
DIPHENYLAMINE INDICATOR

Test No.	Ml. stock FeCl_3 solution taken	Ml. $\text{K}_2\text{Cr}_2\text{O}_7$ solution required	Total volume at start of titration	Fe_2O_3 equivalent of $\text{K}_2\text{Cr}_2\text{O}_7$ gm./ml.
1	2.50	2.81	100 ml.	0.002162
2	2.50	2.67	"	
3	5.00	5.20	"	
4	5.00	5.15	"	0.002292
5	10.00	10.00	"	
6	10.00	10.00	"	0.002370
7	15.00	14.65	"	
8	15.00	14.68	"	0.002425
9	20.00	19.27	"	
10	20.00	19.10	"	
11	20.00	19.33	"	0.002466
12	20.00	19.20	"	
13	25.00	24.20	"	
14	25.00	24.00	"	0.002459
15	35.00	33.20	"	0.002498
16	45.00	42.60	"	0.002504
17	50.00	47.30	"	0.002505
18	73.00	69.03	"	0.002506

Since the concentration of acids and salts, other than the concentration of ferric chloride, was the same in each test it is felt that the results obtained are a fair picture of what happens in many cement mills and testing laboratories using the procedure outlined. To present these data in a form more easily compared with the analysis of cement and raw materials, *Table IV* was calculated from *Table III*. In *Table IV* the figures in the right-hand column would represent the error in per cent. of ferric oxide that would be obtained using a 1-gr. sample of material containing the amount of ferric oxide listed in column 1. It is realised that such a titration would be better conducted

with a constant volume at the end of the titration. It is also realised that if the titration were conducted very slowly toward the end better agreement with the truth might be obtained. However, it is felt that the procedure followed more nearly represents the method employed in the majority of cement testing laboratories.

The stipulation in the specifications of the A.S.T.M. and Federal Government^{3,4} that the dichromate solution be standardised with an amount of sample that "will yield a titration approximately equal to that required by the cement sample in question" would eliminate the error. It is believed that most chemists feel that all cements are nearly enough in the same range to need only one standardisation. The construction of a calibration curve would be feasible, but further tests show that the ferric oxide content of cements may be more conveniently determined by another method.

TABLE IV
ERROR IN FERRIC OXIDE DETERMINATION USING
DIPHENYLAMINE INDICATOR

Fe ₂ O ₃ taken (centigrams)	Fe ₂ O ₃ found (centigrams)	Error (centigrams)
0.59	0.65	+0.06
1.18	1.23	+0.05
2.37	2.37	0.00
3.55	3.48	-0.07
4.74	4.56	-0.18
5.93	5.71	-0.22
8.30	7.87	-0.43
10.67	10.10	-0.57
11.85	11.21	-0.64
17.30	16.36	-0.94

Barium Diphenylamine Sulphonate.

The National Bureau of Standards sample No. 27-B (Sibley iron ore) was used as a standard. Various weights of samples were dissolved in concentrated hydrochloric acid with the aid of stannous chloride solution. An amount of acid was used to combine with the iron and to make the solution approximately normal in free hydrochloric acid on completion of the titration. The reduction of stannous chloride and cooling were performed in the same manner as when using diphenylamine. In order to keep the volume small, 10 ml. of mercuric chloride were added to each sample and the solution was stirred until the excess stannous chloride was completely oxidised. A titrating mixture was prepared by diluting 450 ml. of phosphoric acid (syrupy, 85 per cent.) to one litre with distilled water. An amount of this titrating mixture was added to give approximately 10 per cent. by volume of the titrating mixture on completion of the titration. At least two determinations were made for each weight of sample chosen. In most cases different amounts of indicator were used on duplicate determinations. In all cases correction was made for the indicator used. These

corrections were based on the data given by Sarver and Kolthoff.⁹ The data are listed in *Table V*.

TABLE V
STANDARDISATION OF $K_2Cr_2O_7$ SOLUTION WITH SIBLEY IRON ORE
USING BARIUM DIPHENYLAMINE SULPHONATE AS INDICATOR

Weight of sample taken (gr.)	Weight Fe_2O_3 taken (gr.)	Ml. $K_2Cr_2O_7$ for titration	Indicator correction	Ml. $K_2Cr_2O_7$ for Fe_2O_3	Fe_2O_3 equivalent of $K_2Cr_2O_7$ solution (gr. Fe_2O_3 /ml. $K_2Cr_2O_7$)
0.0273	0.0266	10.75	-0.12	10.63	0.002502
0.0273	0.0266	10.73	-0.12	10.61	0.002507
0.0273	0.0266	10.70	-0.06	10.64	0.002500
0.0273	0.0266	10.67	-0.06	10.61	0.002507
0.0273	0.0266	10.69	-0.06	10.63	0.002502
0.0359	0.0350	14.07	-0.06	14.01	0.002498
0.0359	0.0350	14.07	-0.06	14.01	0.002498
0.0487	0.0475	18.99	-0.06	18.93	0.002509
0.0487	0.0475	19.04	-0.03	19.01	0.002499
0.0615	0.0600	23.98	-0.12	23.86	0.002515
0.0615	0.0600	24.10	-0.03	24.07	0.002493
0.0846	0.0825	33.09	-0.12	32.97	0.002502
0.0846	0.0825	33.01	-0.03	32.98	0.002502
0.1076	0.1050	41.98	-0.12	41.86	0.002508
0.1076	0.1050	41.80	-0.06	41.74	0.002515
0.1230	0.1200	47.90	-0.12	47.78	0.002512
0.1230	0.1200	47.82	-0.06	47.76	0.002513
0.1948	0.1900	75.81	-0.12	75.69	0.002510
0.1948	0.1900	75.80	-0.06	75.74	0.002509
				Average ..	0.002506

The ferric oxide content was determined on the Lehigh Standard Cement sample using the average value (*Table V*) found, with Sibley iron ore, for the strength of the dichromate solution. The data are listed in *Table VI*.

TABLE VI
STANDARDISATION OF LEHIGH STANDARD CEMENT SAMPLE WITH
 $K_2Cr_2O_7$ Solution (1 ml. = 0.002506 gr. Fe_2O_3)

Weight of sample	Ml. $K_2Cr_2O_7$ for titration	Indicator correction	Ml. $K_2Cr_2O_7$ for Fe_2O_3	Per cent. Fe_2O_3 in sample
1 gr.	10.81	-0.12	10.69	2.68
1 gr.	10.80	-0.06	10.74	2.69
1 gr.	10.79	-0.03	10.76	2.70
Average ..				2.69

Further "standardisation" determinations were made on the potassium dichromate solution, using portions of the Lehigh standard sample as a source of ferric oxide. The same considerations were observed for concentration of hydrochloric and phosphoric acid as for the Sibley iron ore determinations. These data are given in *Table VII*. The data of *Tables V* and *VII* are plotted in *Fig. 1*.

TABLE VII
STANDARDISATION OF $K_2Cr_2O_7$ SOLUTION WITH LEHIGH STANDARD
(Lehigh Standard = 2.69 per cent. Fe_2O_3)

Weight of sample taken (gr.)	Weight of Fe^{2+} taken (gr.)	Ml. $K_2Cr_2O_7$ for titration	Indicator correction	Ml. $K_2Cr_2O_7$ for Fe^{2+}	Fe_2O_3 equivalent of $K_2Cr_2O_7$ solution (gr. Fe_2O_3 /ml. $K_2Cr_2O_7$)
0.4461	0.0120	4.90	-0.06	4.84	0.002479
0.4461	0.0120	4.90	-0.06	4.84	0.002479
0.2230	0.0060	2.55	-0.06	2.49	0.002410
0.2230	0.0060	2.52	-0.06	2.46	0.002439
0.1115	0.0030	1.29	-0.06	1.23	0.002439
0.1115	0.0030	1.29	-0.06	1.23	0.002439

Barium diphenylamine sulphonate (0.158 gr. per 100 ml. water) solution was used as the indicator in all these tests. One drop of indicator solution was considered to require 0.015 ml. potassium dichromate solution to be oxidised to the coloured form. A 50-ml. burette was used throughout this series.

Sodium Diphenylbenzidine Sulphonate Indicator.

Tests were made with Sibley iron ore and Lehigh standard sample as described except that a 0.1 per cent. solution of sodium diphenylbenzidine sulphonate¹⁰ was used as an indicator. The method of making the titration was modified as follows. The dichromate solution was added from a weight burette until

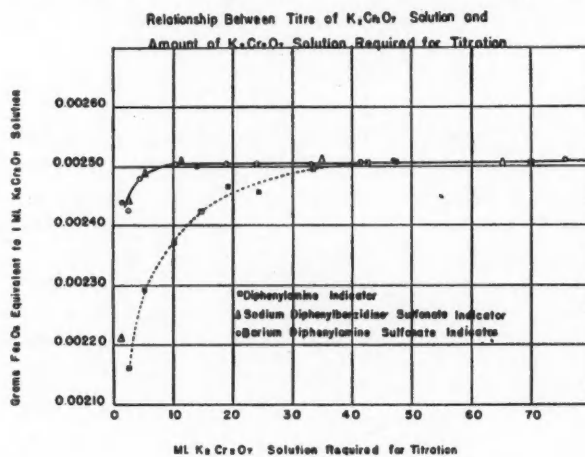


Fig. 1.

a few drops from the end point and the titration completed with a dichromate solution which had been diluted to one-tenth strength and which was added from a volume burette. The weight figures were converted to volume figures to facilitate comparison with data obtained on other indicators. Weights of

dichromate used were corrected to *in vacuo*. The density of the dichromate solution was assumed to be the same as water for the purpose of these calculations. The data are listed in Table VIII. Only one determination was made for each weight of sample. The indicator correction was neglected. The data of Tables V, VII and VIII are plotted in Fig. 1.

TABLE VIII

RELATIONSHIP BETWEEN TITRE OF $K_2Cr_2O_7$ SOLUTION AND AMOUNT OF $K_2Cr_2O_7$ SOLUTION REQUIRED FOR TITRATION USING SODIUM DIPHENYL-BENZIDINE SULPHONATE AS INDICATOR. INDICATOR CORRECTION NEGLECTED.

Weight of sample taken (gr.)	Weight of Fe_2O_3 taken (gr.)	Ml. $K_2Cr_2O_7$ for titration (no correction for indicator)	Gr. Fe_2O_3 equivalent to 1 ml. $K_2Cr_2O_7$ solution
0.08920 (c)	0.00240	1.085	0.002212
0.22300 (c)	0.00600	2.458	0.002441
0.50000 (c)	0.01340	5.403	0.002480
0.02831 (o)	0.02762	11.020	0.002506
0.08975 (o)	0.08756	34.870	0.002511
0.16695 (o)	0.16288	65.090	0.002502

Above data plotted in Fig. 1.

(c) Sample of cement. Lehigh standard sample, $Fe_2O_3 = 2.69$ per cent.

(o) Sample of Sibley iron ore. U.S. Bureau of Standards standard sample No. 27B.

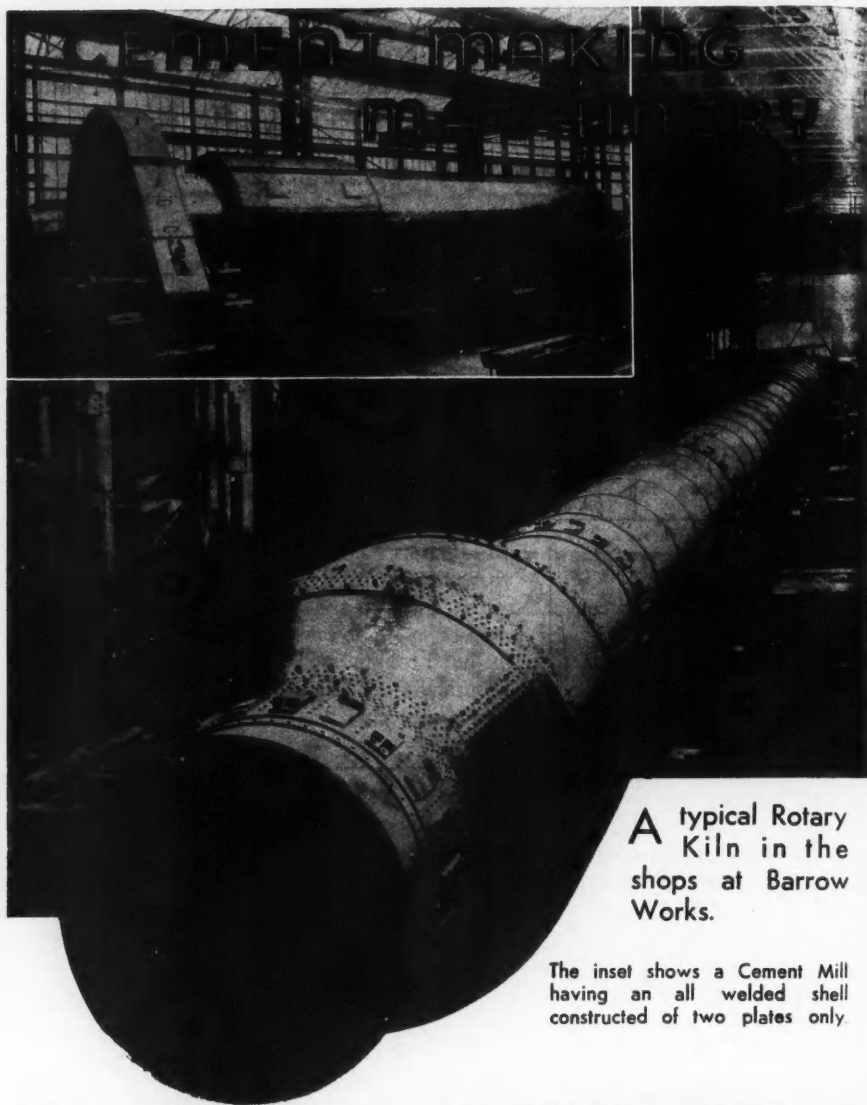
Table IX has been calculated from Tables V and VII to show the error that may be expected, using the proposed method for cements and acid-soluble materials. The figures in the right-hand column would be in per cent. of ferric oxide if a 1-gr. sample of material containing the amount of ferric oxide indicated in the left-hand column were taken for analysis.

Discussion of Results.

Since a fair degree of reproducibility on the same sample by the same analyst is obtainable with diphenylamine, diphenylamine sulphonic acid, and diphenylbenzidine sulphonic acid, it was considered that the relationship between the amount of dichromate used and the ferric oxide equivalent of the dichromate solution would be a good basis for comparison of the indicators.

Fig. 1 shows little choice between sodium diphenylbenzidine sulphonate and barium diphenylamine sulphonate in respect to constancy of titre for various amounts of iron titrated. Both are much superior in this respect to diphenylamine. The change in titre for small amounts of iron is not due to the "drop error" as might have been suspected when using the 50-ml. volume burette. The use of the weight burette in conjunction with a volume burette containing a much-diluted solution virtually eliminates the "drop" error. Kolthoff¹¹ states that more than the theoretical amount of dichromate is necessary to oxidise the iron in solutions of 0.1 normal and less, the deviation increasing with the dilution. This is the probable explanation of the change in titre in this case.

From the standpoint of distinctness of end-point barium diphenylamine sulphonate is much superior to sodium diphenylbenzidine sulphonate, with



A typical Rotary Kiln in the shops at Barrow Works.

The inset shows a Cement Mill having an all welded shell constructed of two plates only.

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diphenylamine a poor third. From the standpoint of accuracy and reproducibility, there is little to choose between barium diphenylamine sulphonate and sodium diphenylbenzidine sulphonate.

The chief disadvantage of barium diphenylamine sulphonate is an appreciable indicator correction, but, if the same amount of indicator is used each time, neglect of the indicator correction introduces a small error within the limits of error inherent in the determination and of no considerable consequence in the analysis of Portland cement. In view of these considerations, barium diphenylamine sulphonate is considered to be the most practical indicator. In addition to increasing the accuracy of the determination, barium diphenylamine sulphonate indicator is soluble in water rather than concentrated sulphuric acid. No titrating mixture requiring the mixing of sulphuric acid and water is necessary. The phosphoric acid may be diluted to any desired concentration with no special precautions. The end-point is such that it may be approached rapidly without danger of over titration when using the proposed method. The use of this method in several laboratories of the Lehigh Portland Cement Co. has met with unqualified approval.

Over the ordinary range of ferric oxide content found in Portland cements the error occasioned by neglecting the indicator correction is small and of the magnitude that seems inherent in the determination. The proposed method for cements neglects this correction and assumes standardisation within the range that is expected. For materials outside the range 0.5 per cent. ferric oxide—20 per cent. ferric oxide, it is expected that the analyst will take the indicator correction into account or vary the weight of sample to bring the titration within the desired range.

The Proposed Method and the Reagents.

Stannous Chloride Solution.—Dissolve 2 gr. of the crystallised salt in four times its weight of a mixture of 3 parts of water and 1 of hydrochloric acid (sp. gr. 1.19). Add scraps of iron-free granulated tin and boil until the solution is clear. Keep the solution in a closed dropping bottle containing metallic tin.

Mercuric Chloride Solution.—Saturated solution. Dissolve about 70 gr. of mercuric chloride in one litre of hot distilled water. Let it cool to room temperature and pour off clear liquid.

Potassium Dichromate Solution.—Dissolve 1.5375 gr. of potassium dichromate per litre of solution.

Titration Solution.—450 ml. phosphoric acid (syrupey, 85 per cent.) diluted to one litre with distilled water.

Indicator Solution.—Dissolve 0.158 gr. barium diphenylamine sulphonate in 100 ml. of water.

Standardisation of Dichromate Solution.—Weigh out an amount of Bureau of Standards sample No. 27-B that will give a titration in the desired range (0.0273 gr.) and place it in a 100-ml. beaker. Add 10 ml. of concentrated hydrochloric acid and digest it on the hot plate at 80 deg. C. to 90 deg. C. until

everything is in solution except a little silica. Solution may be hastened by the addition of the stannous chloride solution, but the amount of stannous chloride solution added should not be sufficient to give a colourless solution. The solution should be a pale yellow when the sample is dissolved. This procedure will offer no difficulty to the analyst after dissolving a few samples. When the sample is in solution the sides of the beaker are washed down with a little hot water, and stannous chloride solution added, one drop at a time with stirring, until the solution is colourless. One drop is added in excess and the beaker and contents cooled by partial immersion in a pan of cold water. To the cold solution are added 10 ml. of saturated mercuric chloride, and the contents of the beaker are stirred for a minute. Eight to 10 ml. of the phosphoric acid reagent and 4 drops of indicator solution are added, and the solution is titrated with dichromate until the reddish-blue colour is permanent. The ferric oxide equivalent of the dichromate solution is calculated according to the equation

$$\frac{\text{Grammes Fe}_2\text{O}_3 \text{ equivalent to } 1 \text{ ml. K}_2\text{Cr}_2\text{O}_7 \text{ solution}}{= \frac{(\text{Wt. of sample}) (\% \text{ Fe}_2\text{O}_3 \text{ in sample})}{(\text{ml. K}_2\text{Cr}_2\text{O}_7 \text{ solution required for titration}) (100)}}$$

* One gramme of the cement is weighed out and transferred into a clean dry 150-ml. beaker. Ten ml. of cold distilled water are added while swirling the beaker. This should result in nearly complete dispersion of the cement in the water. The swirling is continued while 10 ml. of concentrated hydrochloric acid are added and for a few seconds longer. This should result in almost complete



(Defence (General) Regulations, 1939,
No. 56AAA. S.R. & O. 1942 No. 761)

MINISTRY OF WORKS & BUILDINGS

COMPULSORY DISCLOSURE OF SCRAP METAL

EVERY OCCUPIER OF PREMISES in the areas of the United Kingdom specified below must furnish to the Ministry of Works & Buildings a return of any accumulation on those premises of 3 tons or more of metal suitable for scrap. Returns must be made on a prescribed form within 30 days of 14th May, 1942, or of any subsequent day on which such an amount of metal suitable for scrap is brought on the premises.

The areas to which this notice applies are:—

The LONDON CIVIL DEFENCE REGION
The County of ESSEX
The County of DORSET

The County Borough of BRISTOL
The County of NOTTINGHAMSHIRE
The County of MONMOUTHSHIRE

The County Borough of LEEDS
The Counties of EAST, WEST
and MID-LOTHIAN

Returns from other areas will be required in due course

Metal is deemed suitable for scrap if it is, or forms part of any building, structure, machinery, plant or article which is disused, obsolete or redundant, or otherwise serving no immediate purpose.

Aluminium and magnesium, and alloys of either of them, are exempted from the Order.

Under the Order "Premises" means any building or land having an assessment under Schedule A or subject to a valuation for rating.

Returns are NOT required where:—

(a) The Board of Trade certify that the metal is, or forms part of, machinery or plant that is disused or spare in consequence of a concentration scheme approved by them.

(b) The metal forms part of stand-by plant or equipment held by Public Utility Undertakings and essential for the performance of the statutory obligations of those undertakings.

(c) The metal forms part of a machine tool of any of

the descriptions specified in the first schedule to the Control of Machine Tools (No. 9) Order 1941, or a cutting tool of any of the descriptions specified in the first schedule to the Control of Machine Tools (Cutting Tools) (No. 1) Order 1942 or any Order replacing or amending them.

(d) Returns in respect of the metal are already made under the Industry (Records & Information) Orders 1940 and 1941.

★ FORMS on which returns must be made are obtainable from the Director of Demolition and Recovery (Scrap Metal Order), Ministry of Works & Buildings, Sanctuary Buildings, Great Smith Street, London, S.W.1.

solution of the sample. If any lumps remain they should be broken with a stirring rod. The solution is boiled for about one minute or until solution is complete. Prolonged boiling may result in "jelling" of the silica as well as decreasing the amount of acid present.

The iron is reduced by adding stannous chloride solution to the boiling hydrochloric acid solution of the cement. The stannous chloride solution is added drop by drop with constant stirring until the yellow colour of ferric chloride completely disappears. One small drop is added in excess and the contents of the beaker cooled to room temperature by setting the beaker in a pan or beaker containing cold water.

The excess stannous chloride is oxidised by adding rapidly and all at one time 10 ml. of saturated mercuric chloride to the cool solution while stirring. The stirring should be continued for about one minute to ensure completion of the reaction. Ten ml. of the titrating solution and four drops of indicator solution are added. With no further dilution dichromate solution is added from a 25-ml. burette until the colour changes to a red-blue. The titration is best performed over a glass "window" in the bench illuminated from below by a light in such a manner as to pass light through the solution during the titration.

Notes on Method.

The percentage of ferric oxide is calculated according to the equation

$$\% \text{ Fe}_2\text{O}_3 = \frac{\left(\begin{array}{c} \text{(ml. K}_2\text{Cr}_2\text{O}_7 \text{ required)} \\ \text{(for titration)} \end{array} \right) \left(\begin{array}{c} \text{(Fe}_2\text{O}_3 \text{ equivalent of)} \\ \text{(K}_2\text{Cr}_2\text{O}_7 \text{ solution)} \end{array} \right) (100)}{\text{Weight of sample}}$$

Ten ml. of water and 10 ml. of hydrochloric acid are ample to effect solution of the sample and should result in no difficulty unless the boiling is unduly prolonged.

Ten ml. of mercuric chloride solution is in excess of the amount required. However, the reaction between mercuric chloride and stannous chloride is not instantaneous, and sufficient time should be allowed for completion of the reaction. If no silky precipitate of mercurous chloride appears, insufficient stannous chloride has been used and the determination must be discarded. If the precipitate appears dark coloured, too much stannous chloride has been used, the solution was too warm, or the mercuric chloride was added too slowly.

The solution should not be diluted more than that which results from washing down the sides of the beaker at the various stages of the determination. The indicator colour change and the rate and extent of the reaction between ferrous iron and dichromate are affected by concentration and by acidity. The conditions recommended are capable of giving accurate results on samples as low in ferric oxide as 1 per cent. and fair results on samples as low as 0.3 per cent.

Exactly four drops of indicator solution should be used for each determination. The indicator changes colour as the result of oxidation at the expense of the dichromate solution. In other words, the indicator uses up a portion of the dichromate, and the more indicator used the higher the iron content will appear

to be. A drop of the indicator solution will use 0.01 to 0.02 ml. of the dichromate solution. If the same amount of indicator is used for each run as for standardisation, the error caused by neglecting the indicator correction should not exceed 0.01 per cent. ferric oxide over the range encountered in Portland cements.

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